Interlaboratory Study on DecaBDE in Dust within the EU-Project NORMAN

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Introduction

In September 2005, the EU-project NORMAN has been started in order to establish a network of reference laboratories and related organisations dealing with the monitoring of emerging environmental pollutants (http://www.norman-network.de). The network will provide a basis for the exchange of information and data on emerging pollutants between monitoring laboratories, research centres, competent authorities, and end-users across the EU. The main objective of this network is to support risk assessment by ensuring the quality and comparability of data. For that purpose, the network is developing a validation framework specifically designed to support the harmonised optimisation and validation of analytical methods for monitoring emerging pollutants.
In order to test the developed validation protocols and the ability of the network to meet European demands for monitoring of emerging pollutants, various interlaboratory studies will be undertaken.

One of the three case studies to be conducted within the EU-project NORMAN has the aim to test the protocol for method validation at the routine level and to transfer knowledge from expert to routine laboratories. Decabromodiphenyl ether (decaBDE), an emerging pollutant that belongs to the group of brominated flame retardants, seems to be an ideal example for this case study. On the one hand there is the need for monitoring according to the recently completed risk assessment (EUR 20402 EN) and on the other hand there is still a need for improvement in the analysis of decaBDE in many laboratories (de Boer & Cofino 2002, de Boer & Wells 2006). A sequential approach will be followed, starting with expert laboratories that will harmonise the method, followed by a second intercomparison study with monitoring laboratories to test the harmonised method at the routine level.

All laboratories invited to participate in the first round are considered experts in the field of analysis of polybrominated diphenyl ethers (PBDEs) and are involved in the NORMAN project activities. The first round aims at identifying the crucial steps in the analysis of decaBDE. On the basis of the results of this exercise a very detailed method description will be elaborated to enable monitoring laboratories not specialised in the analysis of brominated flame retardants to determine decaBDE in environmental samples with an acceptable accuracy.

Materials and Methods

For the interlaboratory study, the house dust reference material NIST 2585 recently certified for its PBDE content (Stapleton et al. 2006) was chosen as test sample. This reference material is a sterilized, freeze-dried and sieved (< 100 µm) house dust collected from vacuum cleaner bags from homes, motels, and hotels. It contains various polycyclic hydrocarbons, polychlorinated biphenyl congeners, chlorinated pesticides, and polybrominated diphenyl ether congeners. In addition, a standard solution containing BDE-209 in undisclosed concentration was distributed. This solution was prepared by diluting a certified standard solution of decaBDE in toluene purchased by Wellington Laboratories Inc. (Guelph, Ontario, Canada).

Each laboratory used its own analytical methodology. For the final determination GC/MS operated in either electron impact (GC/EI-MS) or negative chemical ionization (GC/NCI-MS) mode was used. Any appropriate extraction and clean-up method were allowed to use. The sample intake was between

0.1 to 0.5 g. Four replicate analyses of each sample were requested. Because of known blank problems in decaBDE analysis, participants were asked to determine four independent blank replicates. All participants agreed upon the use of $^{13}C_{12}$-labelled decaBDE as internal standard. This is regarded a fundamental requirement for reliable analytical results. During the analysis of the test material the participants were also requested to record each single step of the whole procedure and any circumstances that might have influenced the results.

Statistical evaluation of results was carried out using ProLab (quo data Ltd., Dresden, Germany) based on the requirements of the German Standard DIN 38402-42 and ISO 5725-2, respectively.

Results and Discussion

For the determination of PBDEs in environmental samples, a variety of analytical approaches have been published. In general, methods are based on extraction with an organic solvent and clean-up by adsorption column chromatography. Depending on the matrix in which the PBDEs are analysed, additional clean-up steps including gel permeation chromatography (GPC), sulphuric acid and copper treatment may be necessary to remove matrix constituents such as lipids, sulphur etc.. Finally, quantitative and qualitative analyses are carried out using gas chromatography-mass spectrometry (GC-MS).

The variety of possible options to analyse PBDEs is reflected in our study. Results and detailed method descriptions of 6 laboratories from 5 different countries were received. Each laboratory applied a different analytical method. The internal standard $^{13}C_{12}$-BDE-209 was added prior extraction by all participants. However, amounts added ranged from 2 to 1000 ng. Different extraction techniques like accelerated solvent extraction, shaking and ultrasonic extraction were applied using different solvents and mixtures of solvents. Normally, the obtained extracts were purified applying various clean-up techniques. One laboratory did not undertake any clean-up step at all.
The laboratories used non-polar GC columns with a length of 15 m or less, an internal diameter of 0.25 mm, and a film thickness of 0.1 µm. PTV/splitless with or without pressure pulse or splitless injection, predominantly moderate injector and column temperatures < 300 °C were applied. This denotes, that all participants used separation conditions specifically optimised for the analysis of decaBDE in accordance with the recommendations given in the literature (e.g. Covaci et al. 2003, Björklund et al. 2004, Stapelton 2006).

The results of this interlaboratory study were within a narrow range indicating that all laboratories are experienced in the analysis of PBDEs and followed the recommendations on how to recognise and avoid possible sources of errors. A summary of the results is given in Figure 1.

The evaluation of the results of this study did not revealed any significant difference compared to the certified value. One laboratory produced outliers for both samples, the reasons of which have to be analysed. The average recovery for all other laboratories was 107 %. After elimination of outliers the reproducibility and repeatability variation coefficients were less than 10 % for both samples. This study demonstrates that laboratories experienced in the analysis of PBDEs are able to determine decaBDE in the provided dust sample accurately. However, a tendency to slightly higher decaBDE concentrations compared to the certified value was observed.

Recent international interlaboratory studies have shown that until now satisfactory results are difficult to achieve especially for inexperienced laboratories (de Boer & Cofino 2002, de Boer et al. 2005, de Boer & Wells 2006). The Fifth International Laboratory Performance Study on the Analysis of

Brominated Flame Retardants in Environmental Samples organised by QUASIMEME has still shown relatively high CV values (50-60 %) for BDE-209 in sediments, even though advice with regard to specific analytical difficulties, such as blank problems, has repeatedly given (de Boer et al. 2005).

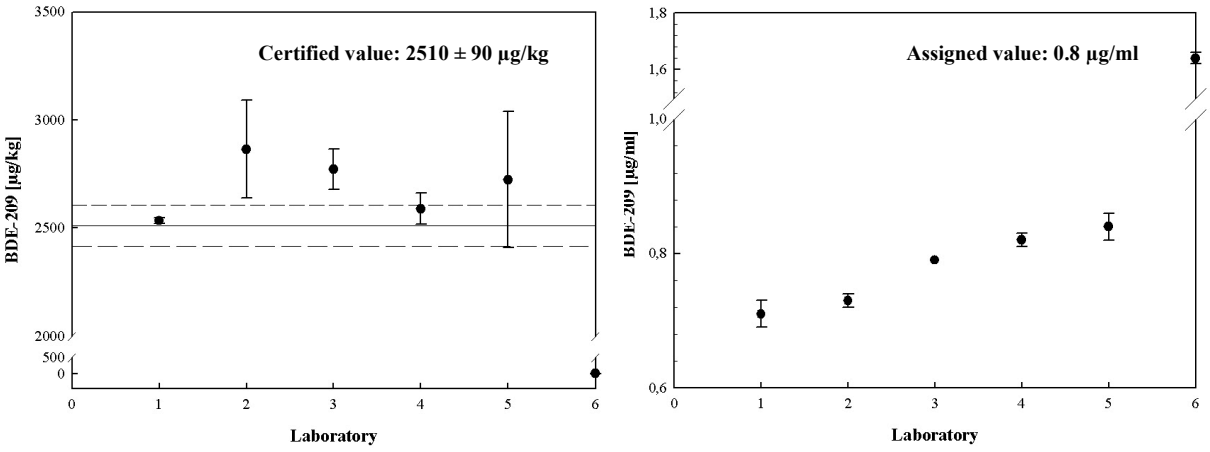

Figure 1: Means of four replicates and standard deviations of decaBDE concentrations in dust (NIST 2585) (to the left) and standard solution (to the right) reported by six laboratories (no elimination of outliers)

Table 1: Performance Characteristics for the NORMAN Interlaboratory Study "Determination of DecaBDE in Dust"

Sample	***l***	***n***	n_{AP} **%**	**x**	s_R	CV_R **%**	s_r	CV_r **%**
Dust	6	24	21	2,685	205	7.65	183	6.80
Solution	6	24	17	0.78	0.06	7.31	0.013	1.67

l Number of laboratories
n Number of single results
n_{AP} Percentage of outliers
x Total mean after elimination of outliers [µg/kg or µg/ml]
s_R Reproducibility standard deviation [µg/kg or µg/ml]
CV_R Reproducibility variation coefficient [%]
s_r Repeatability standard deviation [µg/kg or µg/ml]
CV_r Repeatability variation coefficient [%]

The first evaluation of the present method performance study showed that several methods for extraction and clean-up are appropriate for the determination of decaBDE in dust. The approach to offer various methodological options is also adopted in the International Standard (ISO/DIS 22032) for the determination of PBDE in sediment and sewage sludge. Obviously, the choice of the analytical

method is less important than the experience of the laboratories and the careful control of critical factors like thermal and photochemical degradation of decaBDE as well as blanks. Analytical solutions to avoid these possible errors are described in the literature (Covaci et al. 2003, de Boer & Wells 2006). In view of all the critical factors in the analysis of decaBDE in environmental samples QA/QC measures are of utmost importance. An internal standard, preferably $^{13}C_{12}$-BDE-209 as in the present study, should always be used to compensate for the losses throughout the analytical procedure and for inter-injection fluctuations.

A further discussion with all participating laboratories will give a deeper insight in the applied analytical methods. On the basis of all findings of this method performance study, a detailed method description for the determination of decaBDE in dust will be prepared, which shall be applicable for the second round for routine laboratories.

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